



## Simple method to synthesize high surface area magnesium oxide and its use as a heterogeneous base catalyst

Jonathan K. Bartley<sup>\*</sup>, Chunli Xu<sup>1</sup>, Rhys Lloyd<sup>2</sup>, Dan I. Enache<sup>2</sup>, David W. Knight, Graham J. Hutchings

Cardiff Catalysis Institute, School of Chemistry, Cardiff University, PO Box 912, Cardiff, CF10 3AT, United Kingdom

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### ABSTRACT

High surface area magnesium oxide ( $\sim 250$ – $300 \text{ m}^2 \text{ g}^{-1}$ ) was synthesized via the thermal decomposition of different precursors including  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{MgCO}_3$  and  $\text{MgC}_2\text{O}_4$ . The high surface area MgO displayed exceptionally high catalytic activity for the liquid phase Meerwein–Ponndorf–Verley (MPV) reaction of benzaldehyde with different alcohols. The effect of the calcination temperature and precursor source on the catalytic activity and morphology of MgO has been investigated in detail. It was found that the optimum calcination temperature was  $450^\circ\text{C}$  leading to a high surface area material containing no  $\text{MgCO}_3$  which is the key to obtaining high catalytic activity of MgO for the MPV reaction. The high area MgO catalyst could be reused without loss of catalyst activity. The simplicity of the synthesis method gives this methodology widespread applicability in countless applications that currently use homogeneous base catalysts or stoichiometric bases as reagents.

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### 1. Introduction

Many important synthesis reactions, such as aldolisation, alkylation, Meerwein–Ponndorf–Verley reduction, Wadsworth–Emmons addition, Knoevenagel and Michael condensations can be performed using base catalysts [1–4]. Homogeneous base catalysts, such as alkaline hydroxides and metal alkoxides, are applied in many industrial processes [5–11]. However, the use of these homogeneous base catalysts requires neutralisation and separation from the reaction mixture, leading to loss of catalyst, reduction of the product yields and a number of environmental problems. In recent years, there has been increasing emphasis on the design and use of environmentally-friendly heterogeneous base catalysts to reduce the amount of toxic waste and by-products arising from chemical processes. This has been prompted by stringent environment protection laws and consequently studies of solid base catalysts are becoming increasingly important.

Several solid bases have been reported as being effective in this respect: (i) alkali ion-exchanged zeolites [12,13] and sodium metal clusters in zeolites [14]; (ii) alkali metal ions including alkaline oxides supported on microporous [15] and mesoporous solids

[16], alkali metals supported on alumina ( $\text{Na}/\text{NaOH}/\gamma\text{-A}_2\text{O}_3$ ) [17]; (iii) clay minerals, for example sepiolites [18] and hydrotalcites [19–21]; (iv) non-oxide bases including phosphates [22–25] and nitrides [26,27]; (v) single component catalysts such as alkaline earth solids [28,29]; and (vi) mixed metal oxides, for example magnesium–lanthanum oxide [30]. We have studied tri-glyceride transesterification, Michael addition and Knoevenagel condensation in the presence of a MgO catalyst, and found that activity was dependent on the method of MgO preparation and the test reaction conditions [3,4].

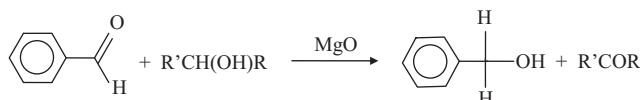
Magnesium oxide (MgO) is a typical basic oxide (Hammett constant,  $H = +26.0$ ) [31] and has the lowest solubility among the alkaline earth oxides. In view of this, we consider that MgO has the potential to be a reusable catalyst, as it may not be lost by leaching into the reaction mixture. Furthermore, MgO is inexpensive and easily obtained and as a result it can be readily applied in large scale manufacture. These characteristics suggest that MgO has potential use in numerous applications in fine and bulk chemical synthesis, but at the present time, it is used only in a small number of reactions. This is primarily because the structure and activity of MgO are affected by the preparation method [2,32–35] and that readily available commercial MgO samples show low surface area (typically  $<20 \text{ m}^2 \text{ g}^{-1}$ ) [36] and hence, low activity. Consequently, as activity is linked to surface area, many preparative methodologies for the synthesis of high surface area MgO have been developed [34–40] such as chemical vapour deposition (CVD) [37], sol–gel procedures [38] and aerogel syntheses [36,39]. However, these methods are relatively complex. As the cost of fabricating a catalyst can be a critical factor in its application few commercial

\* Corresponding author.

E-mail address: [BartleyJK@cf.ac.uk](mailto:BartleyJK@cf.ac.uk) (J.K. Bartley).

<sup>1</sup> Present address: School of Chemistry and Materials Science, Shaanxi Normal University, 199, Chang'an South Street, Xi'an 710062, PR China.

<sup>2</sup> Present address: Johnson Matthey Plc., P.O. Box 1, Belasis Avenue, Billingham, Cleveland, TS23, 1LB, U.K.



**Scheme 1.** MPV reaction of benzaldehyde.

materials have been synthesized in this way. Consequently, we consider that a simpler and more economic preparation method of MgO is still desirable.

In the present work, we systematically studied non-complex methods to synthesise MgO, and observe that the preparation method has a marked effect on both the morphology and surface properties of the final product. We chose the Meerwein–Ponndorf–Verley (MPV) reduction (Scheme 1) as a model reaction and show that using a relatively simple calcination method, high surface area MgO can be obtained that exhibits excellent catalytic activity in MPV reactions and provides a stable reusable base catalyst. The simplicity of the synthesis method, when compared with sol–gel or CVD procedures, gives this methodology widespread applicability in countless applications that currently use homogeneous base catalysts or stoichiometric bases as reagents.

## 2. Experimental

### 2.1. Preparation of MgO catalysts

MgO was prepared from a number of different precursors (see Table 1 for details). Commercially available magnesium hydroxide (Fluka, 99%), basic magnesium carbonate ( $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ , ≥40% MgO; Fluka) and magnesium carbonate ( $\text{MgCO}_3$ , Acros Organics, 40–45% MgO) were calcined in static air. The materials were designated as MgO-COH, MgO-CBC and MgO-CC respectively.

Rehydrated  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  was obtained from the commercially available basic magnesium carbonate ( $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ ; 25 g), which was suspended in distilled water (750 ml), stirred at 70–90 °C for 30 min., filtered, dried (90 °C; 24 h) and then recalcined. This material was designated as MgO-RBC.

Commercially available magnesium hydroxide (Fluka, 99%; 21.8 g) was calcined at 600 °C for 2 h. The magnesium oxide

**Table 1**  
BET surface area of MgO materials.

Catalyst	Precursor	Calcination conditions	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )
MgO-CBC	Commercial $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ (Fluka)	800 °C, 2 h	20
		700 °C, 2 h	59
		600 °C, 12 h	79
		600 °C, 2 h	126
		500 °C, 2 h	206
		475 °C, 2 h	281
		450 °C, 2 h	288
		425 °C, 2 h	342
		400 °C, 2 h	302
		375 °C, 2 h	56
		350 °C, 2 h	23
		No calcination	14
MgO-RBC	Rehydrated $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$	450 °C, 2 h	296
MgO-CC	Commercial $\text{MgCO}_3$ (Acros Organics)	450 °C, 2 h	229
MgO-COH	Commercial $\text{Mg}(\text{OH})_2$ (Fluka)	450 °C, 2 h	58
MgO-ROH	Rehydrated $\text{Mg}(\text{OH})_2$	450 °C, 2 h	287
MgO-FOH	Freshly-prepared $\text{Mg}(\text{OH})_2$ ( $\text{MgSO}_4 + \text{KOH}$ )	450 °C, 2 h	245
MgO-OX	$\text{MgC}_2\text{O}_4$	450 °C, 2 h	312

obtained (10 g) was rehydrated by refluxing in distilled water (125 ml) for 3 h. The resultant solid, denoted as rehydrated  $\text{Mg}(\text{OH})_2$ , was dried and then calcined. This material was designated as MgO-ROH.

Freshly prepared magnesium hydroxide, was obtained by precipitating  $\text{MgSO}_4$  solution (250 ml; 1.0 M) with KOH solution (250 ml; 1.0 M). The resulting mixture was aged at room temperature for 3 h, filtered, washed five times with distilled water, dried (90 °C; 24 h) and then calcined. This material was designated as MgO-FOH.

MgO was also obtained by calcination of magnesium oxalate ( $\text{MgC}_2\text{O}_4$ ).  $\text{MgC}_2\text{O}_4$  was prepared following the method described by Putanov et al. [40]. Magnesium oxalate was precipitated from a saturated aqueous solution of  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  using an aqueous solution of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . The saturated aqueous solution of  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was made by adding  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (53.6 g) to distilled  $\text{H}_2\text{O}$  (50 ml). The aqueous solution of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  was prepared by diluting  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (31.5 g) with distilled  $\text{H}_2\text{O}$  (200 ml). The magnesium oxalate was precipitated from moderately heated magnesium acetate solutions at 40 °C and immediately filtered. The precipitate was dried at 90 °C for 24 h. The resulting material was calcined at various temperatures in static air. This material was designated as MgO-OX.

All calcinations were conducted in the range of 200–800 °C for 2 h in static air with a ramp rate of 10 °C min<sup>-1</sup>. After calcination, the temperature of the furnace was decreased to 280 °C and the sample was recovered and stored in a desiccator. Freshly prepared samples of MgO were used for all catalyst evaluations.

### 2.2. Characterisation methods

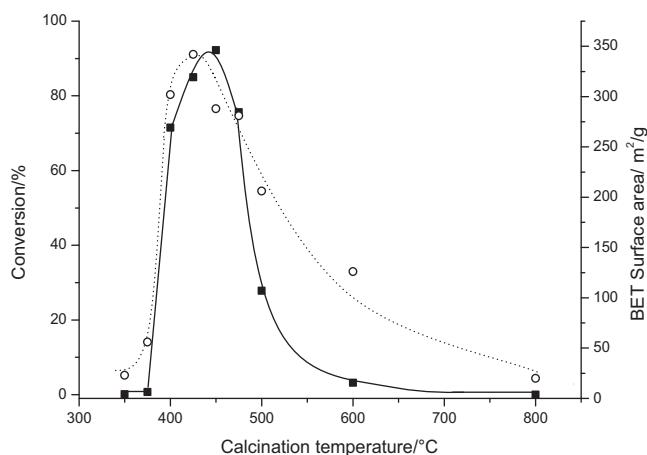
Powder X-ray diffraction was performed using an ENRAF Nonius FR590 X-ray powder diffractometer (Cu-K $\alpha$  source) fitted with an Inel CPS 120 position sensitive detector. BET surface area measurements using nitrogen adsorption were carried out using a Micromeritics Gemini 2360 surface area analyser. TGA experiments were conducted using a TA Instruments Ltd SDT Q600 thermal analysis machine under a flow of nitrogen, with a heating rate of 20 °C min<sup>-1</sup>. SEM micrographs were obtained using FEI XL30 ESEM FEG machine.  $\text{CO}_2$  adsorption was measured using a Thermo Electron Corporation TPDRO 1100 Series instrument fitted with a thermal conductivity detector. Pulsed  $\text{CO}_2$  adsorption measurements in argon were performed at 35 °C.

### 2.3. Catalyst testing

Benzaldehyde (0.006 mol, Aldrich), alcohol (0.12 mol) and the catalyst (0.5 g) were placed in a two-necked flask and heated under reflux conditions. Samples were taken at specified times after reaching the reaction temperature and were analysed using a PerkinElmer Autosystem XL GCMS equipped with a DB-1 column. Carbon mass balances were typically 98–102%.

## 3. Results and discussion

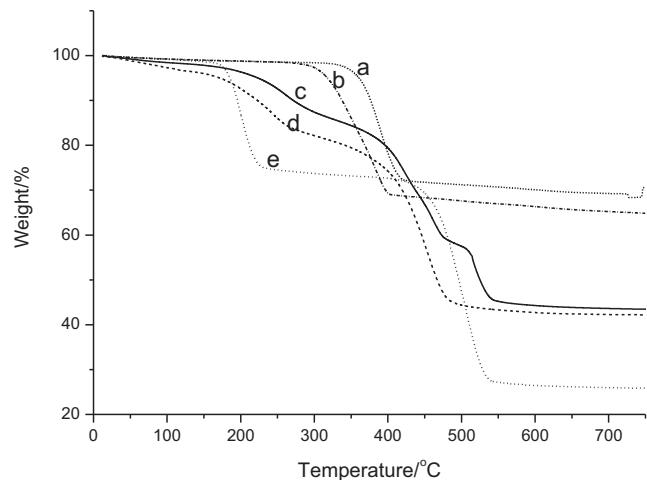
To determine the influence of the calcination temperature on the catalytic activity of the MgO samples, commercially available  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  was calcined at different temperatures between 350 °C and 800 °C and then tested as a catalyst for the reaction of benzaldehyde with 2-butanol. Fig. 1 shows the conversion after 5 min reaction as a function of the calcination temperature. MgO calcined at 450 °C was found to be the most active catalyst. When the calcination temperature was 400–475 °C, >70% conversion was achieved after five minutes reaction, whereas, a low level of activity was observed when the calcination temperature was either <350 °C or >600 °C.



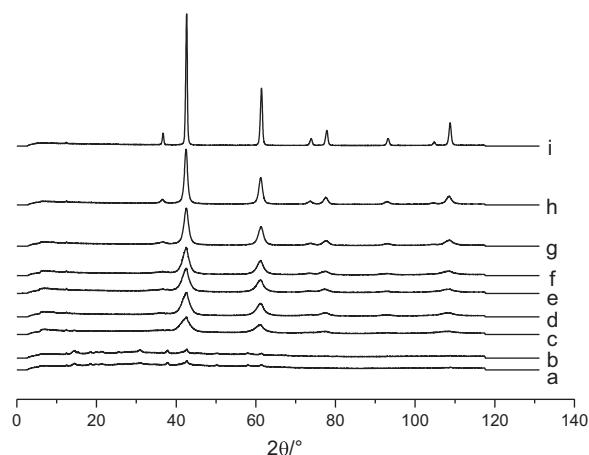
**Fig. 1.** Activity for the MPV reaction of benzaldehyde and 2-butanol after 5 min over MgO catalysts derived from commercially available  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  and their BET surface area as a function of calcination temperature. Key: (■) conversion; (○) BET surface area.

TGA shows the temperatures at which the MgO precursors decompose when heated in a controlled environment (Fig. 2). Water is removed from the precursors between 250 and 400 °C, whereas carbon dioxide is lost between 325 and 550 °C. The thermal pre-treatment resulted in a change in the XRD pattern, caused by the removal of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from the starting material  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  (Fig. 3). The diffraction patterns of the samples heated at temperatures  $<375$  °C contained reflections that could all be assigned to  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  (Fig. 3a–b), while those activated at temperatures  $>400$  °C displayed additional reflections characteristic of MgO (Fig. 3c–i), which became more crystalline with increasing calcination temperature as the  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  reflections decreased. Representative enlargements of the XRD patterns (Fig. 4) shows that after calcination at 450 °C for 2 h the material comprised MgO as the major phase and  $\text{MgCO}_3$  as a minor phase whereas a single MgO phase was observed after calcination at  $>600$  °C for 2 h.

The changes observed in the XRD patterns (Figs. 3 and 4) coincided with a change in the catalytic activity (Fig. 1). Calcination at 375 °C did not lead to the formation of MgO, and, consequently, the catalyst activity was very low. The best catalyst performance was obtained for calcination temperatures between 400 and 475 °C, when a poorly crystalline high surface area MgO was present



**Fig. 2.** TGA curves of MgO precursors: (a) rehydrated  $\text{Mg}(\text{OH})_2$ ; (b) commercial  $\text{Mg}(\text{OH})_2$ ; (c)  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ ; (d)  $\text{MgCO}_3$ ; (e)  $\text{MgC}_2\text{O}_4$ .

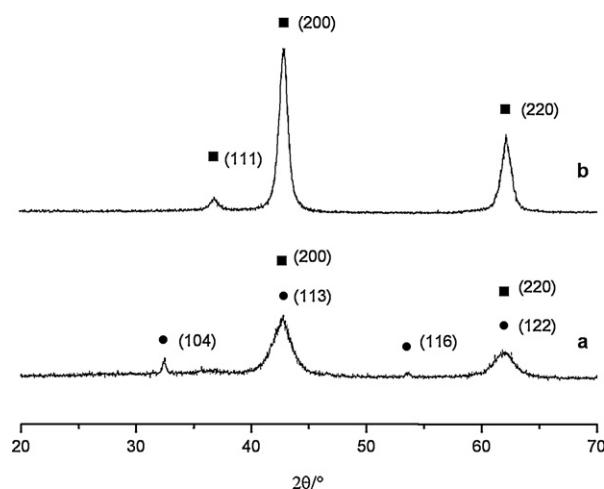


**Fig. 3.** XRD patterns from the materials obtained by calcining commercially available  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  at different temperatures: (a) 350 °C; (b) 375 °C; (c) 400 °C; (d) 425 °C; (e) 450 °C; (f) 475 °C; (g) 500 °C; (h) 600 °C; (i) 800 °C.

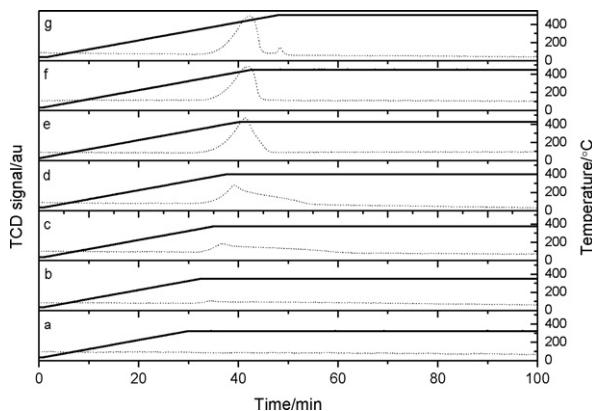
(Figs. 3 and 4, Table 1). The increase in calcination temperature led to a decrease in catalyst activity as the MgO became more crystalline and the BET surface area decreased. It is clear that the surface area plays a key role in determining the activity of the catalysts. However, the material with the highest surface area did not show the best activity, so other factors are clearly influencing the performance.

To investigate how the strength and number of the basic sites changed with temperature,  $\text{CO}_2$  adsorption experiments were carried out on MgO-COH. 40 mg of the precursor was calcined *in situ* prior to analysis and then cooled to 35 °C in argon. The number of basic sites was calculated by pulsing  $\text{CO}_2$  at 35 °C assuming that one molecule of  $\text{CO}_2$  adsorbs at a single basic site. To determine the relative strength of the basic sites, temperature programmed desorption (TPD) of  $\text{CO}_2$  was performed in argon following saturation at 35 °C.

In Fig. 5 the TCD response during the *in situ* calcination of  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  at different temperatures is shown. The decomposition of  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  can be first seen to occur at 350 °C, resulting in the loss of  $\text{CO}_x$  and the generation of MgO. Increasing the temperature above 350 °C results in a higher fraction of  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  decomposing and by 425 °C the size of



**Fig. 4.** Enlargements of XRD patterns from the materials obtained by calcining commercially available  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  at: (a) 450 °C; (b) 600 °C. Key: (■) MgO; (●)  $\text{MgCO}_3$ .



**Fig. 5.** *In situ* calcinations of  $(\text{MgCO}_3)_4\text{-Mg(OH)}_2$  in  $10 \text{ ml min}^{-1}$  air, with a  $10^\circ\text{C min}^{-1}$  heating ramp at: (a)  $325^\circ\text{C}$ ; (b)  $350^\circ\text{C}$ ; (c)  $375^\circ\text{C}$ ; (d)  $400^\circ\text{C}$ ; (e)  $425^\circ\text{C}$ ; (f)  $450^\circ\text{C}$ ; (g)  $500^\circ\text{C}$ . Key: TCD signal (thin lines); temperature (thick lines).

**Table 2**

Number and proportion of basic sites in materials obtained from calcining  $(\text{MgCO}_3)_4\text{-Mg(OH)}_2$  at different temperatures.

Calcination temperature ( $^\circ\text{C}$ )	Number of basic sites ( $\mu\text{mol CO}_2/\text{mol Mg}$ )	Proportion of basic sites (%)	
		50–225 $^\circ\text{C}$	255–425 $^\circ\text{C}$
300	0.33	–	–
325	1.99	–	–
350	3.59	44	56
375	4.01	39	61
400	3.16	27	73
425	2.57	28	72
450	2.19	34	66
475	1.66	32	68
500	1.76	42	58
600	1.10	58	42

the  $\text{CO}_2$  peak is constant indicating complete decomposition of the carbonate at this temperature.

The effect of the structure on the basic properties of the  $(\text{MgCO}_3)_4\text{-Mg(OH)}_2$  calcined between  $300$  and  $600^\circ\text{C}$  is given in Table 2 and shown in Fig. 6. For all catalysts it was apparent that there were two distinct maxima in the desorption profile at around  $150^\circ\text{C}$  and  $320^\circ\text{C}$ . Based on this observation these two regions of desorption were assigned as weakly basic ( $50$ – $225^\circ\text{C}$ ) and strongly basic ( $225$ – $425^\circ\text{C}$ ) sites. If the material was calcined at or below

$325^\circ\text{C}$  very few basic sites were detected. This is unsurprising as during the calcination no decomposition of the carbonate is observed, whereas during the TPD experiment there was a large increase in the signal at  $\sim 350^\circ\text{C}$  as the carbonate started to decompose. At higher *in situ* calcination temperatures there was a large increase in the number of basic sites which reached a maximum at  $375^\circ\text{C}$  and then decreased with increasing calcination temperature (Table 2, Fig. 6). The relative proportion of strongly basic sites, as indicated by the fraction of  $\text{CO}_2$  desorbing above  $225^\circ\text{C}$  was found to be higher for materials calcined between  $400^\circ\text{C}$  and  $475^\circ\text{C}$ .

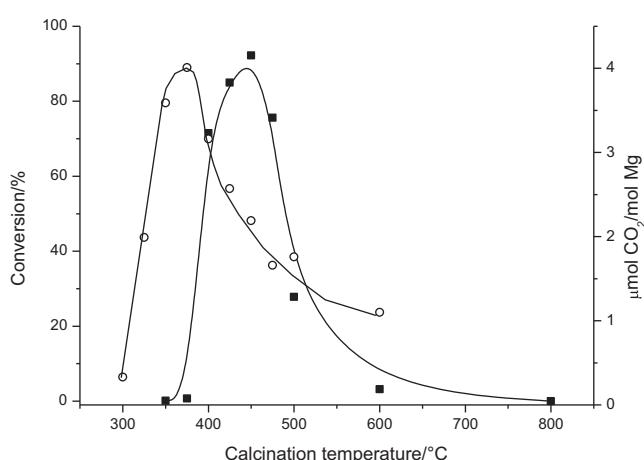
It is proposed that at  $375^\circ\text{C}$  a significant proportion of the  $(\text{MgCO}_3)_4\text{-Mg(OH)}_2$  precursor has decomposed to generate a high surface area, disordered  $\text{MgO}$  with a high number of very basic defect sites. However, calcination at higher temperature leads to bulk decomposition and an exothermic reaction which is considered to result in the removal of basic defect sites and a decrease in surface area [41–44]. At higher temperatures the disordered strong basic sites are removed as the  $\text{MgO}$  becomes more crystalline leading to a decrease in the proportion of strong basic sites.

Fig. 6 shows the catalyst activity and the number of basic sites as a function of temperature. It can be seen that although the general trend is the same as for the surface area, with a sharp increase in the number of sites to a maximum followed by a gradual decrease as the calcination temperature is increased, the two maxima are not observed at the same calcination temperature.

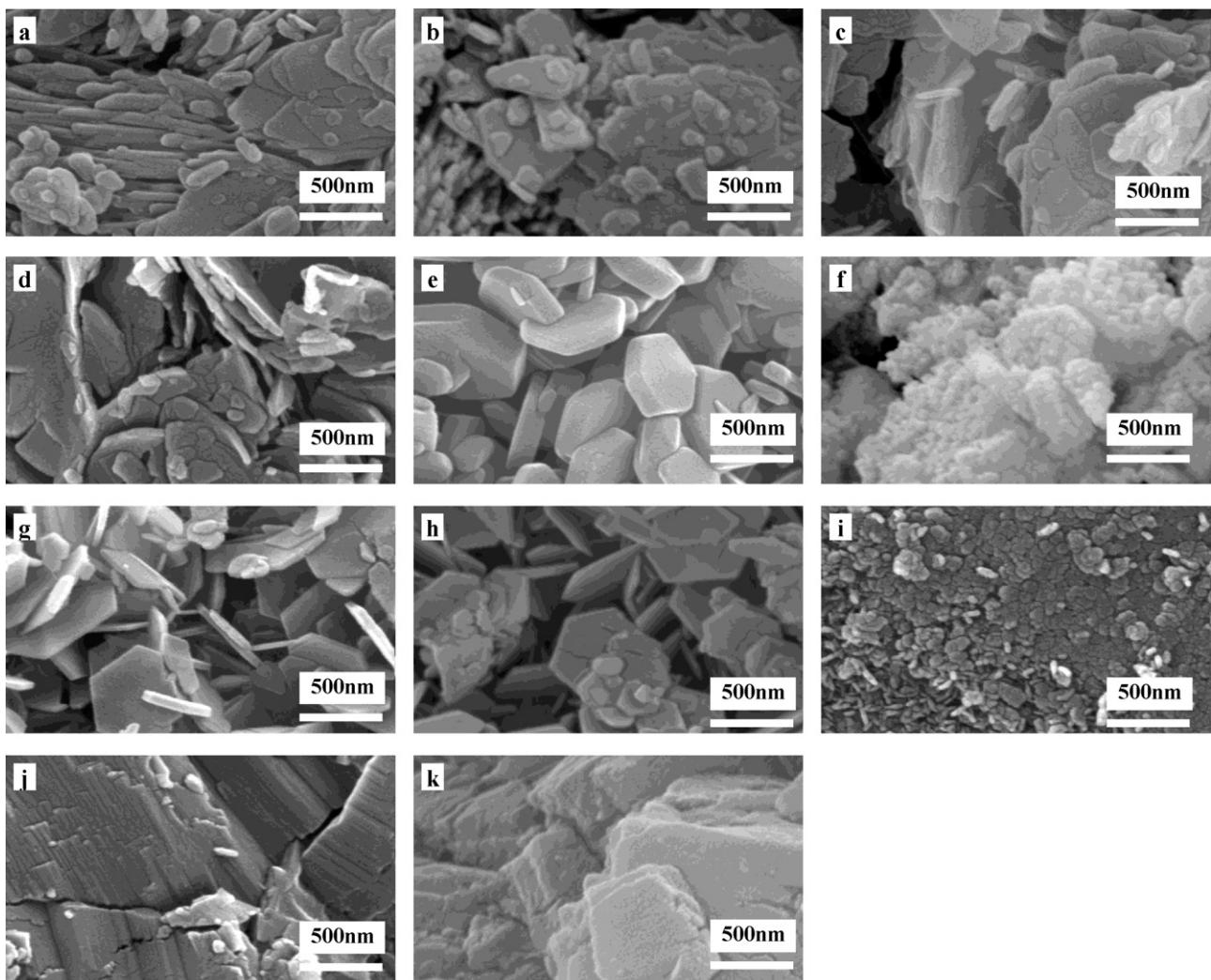
The difference in the optimum calcination temperature required to generate the maximum number of defect sites, surface area and catalytic activity is considered to be due to the different calcination conditions used. Parameters such as atmosphere, flow rate, heating ramp, and sample size, have all been reported to effect the decomposition process [41]. The *in situ* calcination prior to the TPD experiments was carried out with gas flow through a  $40\text{ mg}$  bed of sample (which is not sufficient to determine the surface area of these materials), whereas the calcinations before testing were carried out on  $25\text{ g}$  batches contained in a calcination boat in a tube furnace. This makes it difficult to compare the calcination temperatures and surface areas of the samples in the different experiments directly. However, the onset of carbonate decomposition can be used to analyse differences in the heating regimes of the different samples.

For the calcinations carried out *in situ* before the TPD experiment, the decomposition to the carbonate can be monitored by integrating the TCD signal during the calcination (Fig. 5). The maximum number of basic sites was observed for the material calcined at  $375^\circ\text{C}$  which has  $\sim 70\%$   $(\text{MgCO}_3)_4\text{-Mg(OH)}_2$  decomposition. However, the sample calcined at  $375^\circ\text{C}$  in the tube furnace prior to catalyst testing does not seem to contain  $\text{MgO}$  from the XRD pattern (Fig. 3b) and hence, has a low activity for the MPV reaction (Fig. 1). This makes a direct correlation between the number of basic sites and the surface area and activity difficult. Despite the differences in calcination conditions, combining the information gained from the surface area measurements, the TPD and TGA experiments and the catalyst testing data the properties that make the best basic catalyst can be determined.

At low temperature there was no decomposition of  $(\text{MgCO}_3)_4\text{-Mg(OH)}_2$ , no basic sites were detected on the catalyst and hence the surface area and activity were low. As the temperature was increased the  $(\text{MgCO}_3)_4\text{-Mg(OH)}_2$  began to decompose leading to an increase in surface area and an increase in the number of basic sites as  $\text{MgO}$  defect sites are created. The maximum surface area does not correlate exactly with the highest activity catalyst obtained (Fig. 1) and the removal of carbonate is also a crucial factor. From the TPD experiments the highest number of basic sites correlates to a partially decomposed material. As the calcination temperature was increased complete decomposition



**Fig. 6.** Activity for the MPV reaction of benzaldehyde and 2-butanol after 5 min over  $\text{MgO}$  catalysts derived from commercially available  $\text{MgCO}_3\text{-Mg(OH)}_2$  and the number of basic sites determined by  $\text{CO}_2$  adsorption as a function of calcination temperature. Key: (■) conversion; (○) amount of  $\text{CO}_2$  adsorbed.



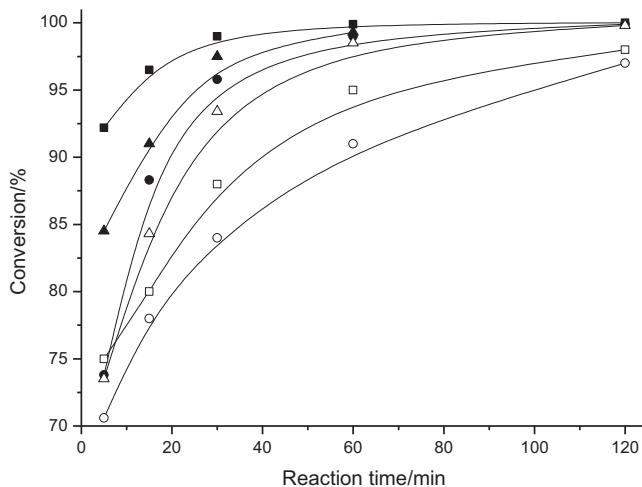
**Fig. 7.** SEM images of the MgO precursors and catalysts obtained via calcination at 450 °C for 2 h: (a)  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ ; (b) MgOCBC; (c)  $\text{MgCO}_3$ ; (d) MgO-CC; (e) commercially available  $\text{Mg}(\text{OH})_2$ ; (f) MgO-COH; (g) rehydrated  $\text{Mg}(\text{OH})_2$ ; (h) MgO-ROH; (i) MgO-FOH; (j)  $\text{Mg}_2\text{C}_2\text{O}_4$ ; (k) MgO-OX.

of the  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$  occurs to form a more crystalline MgO and the surface area and number of basic sites both decreased. There also seems to be a correlation between the strength of the basic sites and surface area. A greater proportion of strong basic sites were found on high surface area, disordered MgO, compared with the highly crystalline, low surface area cubic MgO obtained at high calcination temperatures.

MgO was prepared by calcining a range of precursors at 450 °C (Table 1). SEM images of the MgO materials and precursors (Fig. 7) reveal that the size and morphology of the catalysts produced are very strongly influenced by the morphology of the catalyst precursor, which is typically retained during the calcination procedure. All the samples, except that derived from commercial  $\text{Mg}(\text{OH})_2$  (MgO-COH), were found to have a high surface area. However, after refluxing the MgO-COH material in water followed by recalcination produced a material (MgO-ROH) with high surface area (Table 1). The precursors of both materials consist of hexagonal discs (Fig. 7e and g) and after calcination MgO-ROH (Fig. 7h) remained as hexagonal plates reminiscent of the hydroxide precursor. In contrast, there was a big difference between the morphology of MgO-COH (Fig. 7f) and its precursor (Fig. 7e). It has been reported previously that the morphology of MgO is dependent upon the starting material and the thermal pre-treatment conditions [45]. In this study, MgO-ROH and MgO-COH were prepared by calcining their

corresponding precursors under the same conditions. Therefore, the morphological differences between the MgO-ROH and MgO-COH may be attributed to the use of different precursors. Schwank found that impurities have a significant influence on the morphology of MgO which was produced by dehydration of  $\text{Mg}(\text{OH})_2$  [46]. It is possible that the difference observed in the activity of the two materials is due to an impurity in the commercial sample which is removed during the water reflux step, leading to a high surface area MgO after calcination of the rehydrated precursor. This impurity is likely to be  $\text{Cl}^-$  ions that are commonly present in commercial  $\text{Mg}(\text{OH})_2$  that is typically manufactured via precipitation from brine [47].

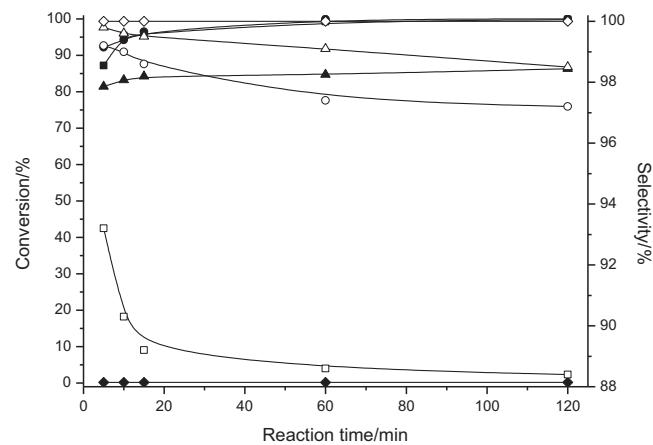
To study the effect of the different precursors on the catalyst activity, the MgO materials obtained using calcination at 450 °C, were tested as catalysts for the MPV reduction of benzaldehyde with 2-butanol. The results are shown in Fig. 8 (conversion) and Fig. 9 (selectivity to benzyl alcohol). All of the MgO materials were found to be initially selective (>93%), and all were active (>90% conversion after 1 h) apart from the low surface area MgO-COH (<1% conversion after 3 h). The main by-product arose from an aldol condensation between benzaldehyde and butanone and the catalysts with lower selectivities (MgO-FOH and MgO-OX) showed a considerable drop in selectivity with time due to this secondary reaction.



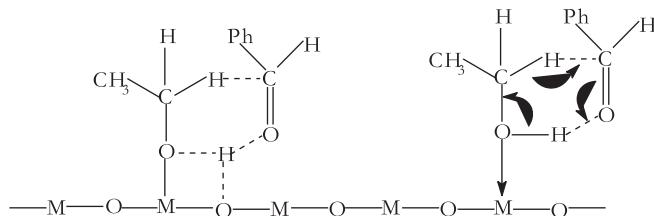
**Fig. 8.** Activity for the MPV reaction of benzaldehyde with 2-butanol over different MgO catalysts: (■) MgO-CBC; (●) MgO-RBC; (○) MgO-CC; (▲) MgO-ROH; (□) MgO-FOH; (△) MgO-OX.

Although most of the catalysts exhibited a high activity for the MPV reaction, MgO-COH had a low activity, which is consistent with its low surface area. MgO-COH and MgO-ROH were prepared from the same parent  $\text{Mg}(\text{OH})_2$  but using a different procedure. MgO-COH was obtained from the direct calcination of commercially available  $\text{Mg}(\text{OH})_2$ , while MgO-ROH was obtained from the calcination of rehydrated  $\text{Mg}(\text{OH})_2$  (commercial  $\text{Mg}(\text{OH})_2$  which had been refluxed in water). The preparation procedure has a direct influence on the surface area of MgO-COH and MgO-ROH ( $\text{MgO-ROH} = 287 \text{ m}^2 \text{ g}^{-1}$ ,  $\text{MgO-COH} = 58 \text{ m}^2 \text{ g}^{-1}$ ) and consequently the activity of the catalysts. However, when the conversion per unit area of catalyst is calculated MgO-ROH is still more active. This indicates that the surface area is not the only factor responsible for the activity, and the water reflux step has additional benefits.

Fig. 10 shows the results obtained from the reaction of benzaldehyde with different alcohols over MgO-CBC. With the exception of 2-methyl-2-propanol, all other substrates yielded a high reaction rate and selectivity. It was found that 2-butanol had a higher selectivity than 1-butanol, which is in agreement with the finding of Figueras [1]: *i.e.* the best hydrogen donors are secondary alcohols with primary alcohols yielding aldehydes which are more



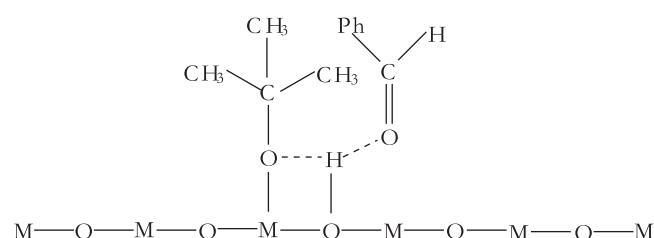
**Fig. 10.** Conversion and selectivity to benzyl alcohol data for the MPV reaction of benzaldehyde with different alcohols over MgO-CBC: (■) 1-butanol; (●) 2-butanol; (▲) 2-methyl-1-propanol; (◆) 2-methyl-2-propanol. Solid symbols refer to conversion, open symbols refer to selectivity.



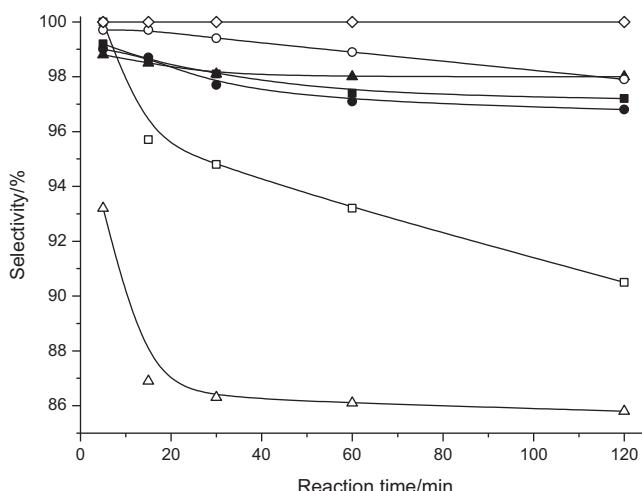
**Scheme 2.** Mechanism of the MPV reaction studied.

prone to undergo cross-aldol condensations and Tishchenko reactions with the substrate. For 2-methyl-2-propanol the selectivity of the reaction was high, but the conversion was only 2%. These catalytic activity results can be explained by a mechanism similar to that proposed previously (Scheme 2) [48], where the hydrogen transfer is a concerted process that takes place *via* a six-member intermediate formed between the alcohol and benzaldehyde. The rate-determining step of the process is considered to be related to the interaction of the alcohol with the basic site, which dissociates to the corresponding alkoxide. In the proposed scheme the surface-adsorbed alkoxide, formed from the alcohol, transfers a hydride ion that attacks the carbonyl group. For 2-methyl-2-propanol, no hydrogen is available to form a six-member intermediate, which explains the low conversion (Scheme 3).

We have compared the performance of MgO-CBC with best previously reported literature studies of simple oxide catalysts for the MPV reaction (Table 3) [49]. CaO was found to be the most active catalyst from five heterogeneous base catalysts, including MgO prepared from commercially available  $\text{Mg}(\text{OH})_2$ , as well as  $\text{CaO}/\text{Al}_2\text{O}_3$ ,  $\text{MgO}/\text{Al}_2\text{O}_3$  and  $\text{Mg}/\text{Ga}_2\text{O}_3$  from the corresponding hydrotalcite precursors. From the comparative data presented in Table 3, it is clear that MgO prepared by the methodology we describe gave a superior catalytic performance for the MPV reaction.



**Scheme 3.** Intermediate for the reaction with 2-methyl-2-propanol.



**Fig. 9.** Selectivity to benzyl alcohol for the MPV reaction of benzaldehyde with 2-butanol over different MgO catalysts: (■) MgO-CBC; (●) MgO-RBC; (○) MgO-CC; (◇) MgO-COH; (▲) MgO-ROH; (□) MgO-FOH; (△) MgO-OX.

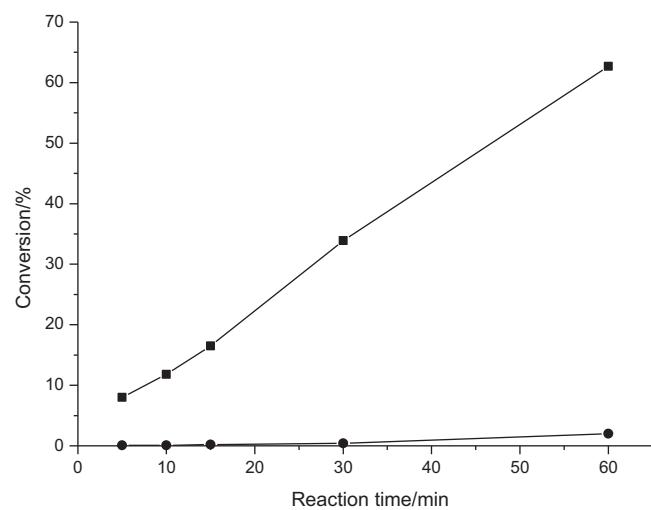
**Table 3**

Catalytic activity and selectivity of MgO-CBC compared with literature data [49].

Entry	Alcohol	Reaction time	Conversion	Selectivity
1	2-butanol	5 min	92.2%	99.2%
2	2-butanol	1 h	99.9%	97.4%
3	2-butanol <sup>a</sup>	10 h	98.7%	90.3%
4	1-butanol	5 min	87.2%	93.2%
5	1-butanol	1 h	99.3%	88.6%
6	1-butanol <sup>a</sup>	10 h	75.2%	58.6%

<sup>a</sup> Reaction conditions: 0.003 mol benzaldehyde; 0.06 mol alcohol; reflux temperature; 1 g CaO [49].

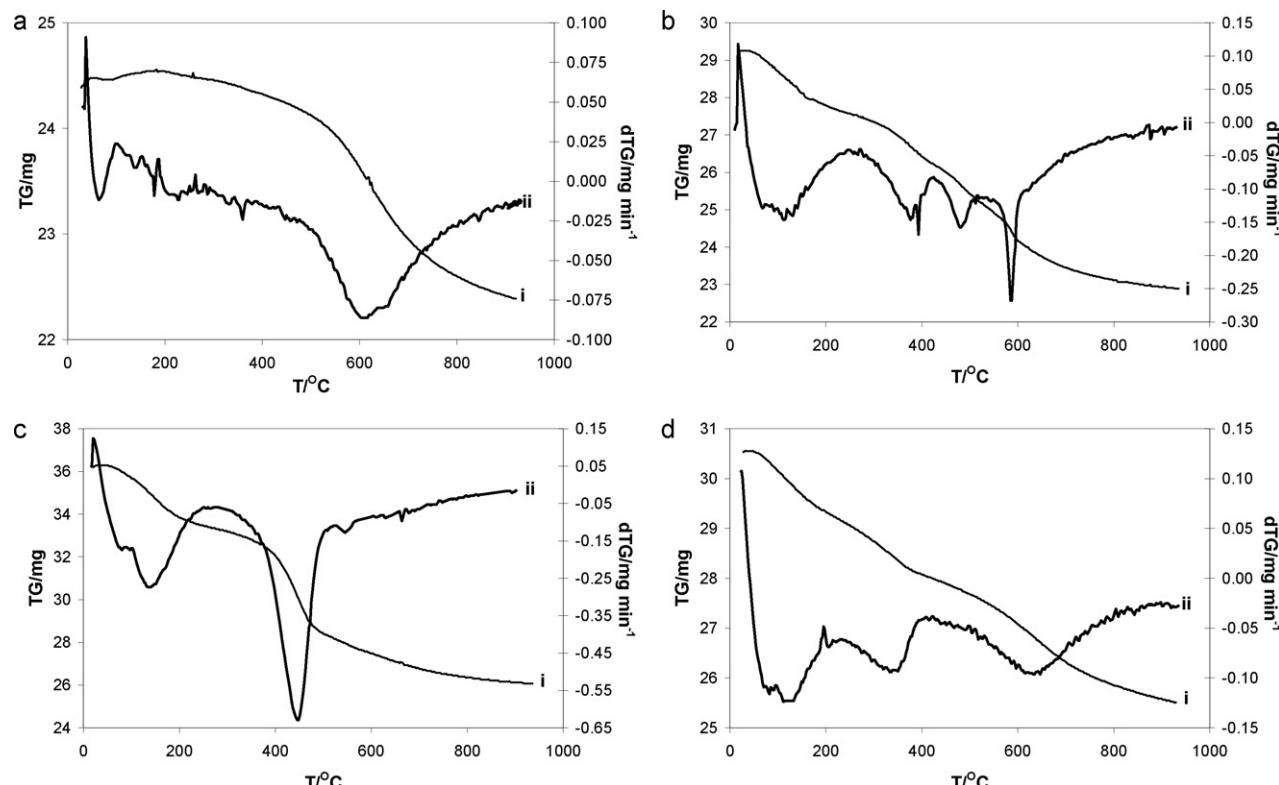
We observed that MgO catalysts rapidly deactivate if they are left exposed to the atmosphere and hence, all the reactions were performed using freshly calcined materials. Fig. 11 shows the catalytic results for freshly calcined MgO (cooled down to room temperature in the furnace) and the same sample having been left in contact with the atmosphere at room temperature for an additional 5 h. The activity of the freshly calcined MgO sample was higher than the material exposed to the atmosphere for 5 h, but lower than the material treated in the standard way (*i.e.* removed from the furnace at 280 °C and placed in a desiccator, Fig. 8, MgO-CBC). It was thought that this decrease in activity of MgO observed could be due to the adsorption of CO<sub>2</sub> and/or H<sub>2</sub>O onto the catalyst surface. To test this hypothesis TGA and DTG of MgO cooled down under different conditions were performed (Fig. 12). MgO cooled down to 280 °C and placed in a desiccator (Fig. 12a) showed a weight loss at around 520 °C due to the decomposition of a small amount of MgCO<sub>3</sub> left in the sample. However, all of the other three samples showed a weight loss below 520 °C, indicating that the other methodologies lead to adsorption of CO<sub>2</sub> and/or H<sub>2</sub>O onto the MgO surface. The MgO materials cooled to room temperature in air (Fig. 12b) and in a CO<sub>2</sub>/H<sub>2</sub>O mixture (Fig. 12c) showed an additional weight loss at ~425 °C due to adsorbed CO<sub>2</sub> and low



**Fig. 11.** The effect of exposure to air on the activity of the MgO-CBC catalyst for the MPV reaction of benzaldehyde with 2-butanol. Key (■) freshly calcined; (●) open to air for 5 h.

temperature weight loss at ~100 °C due to H<sub>2</sub>O which was also present for the material cooled in N<sub>2</sub>/H<sub>2</sub>O (Fig. 12d). The results show that the MgO can readily adsorb H<sub>2</sub>O and CO<sub>2</sub> which can greatly reduce the activity (Fig. 11). In order to achieve a good catalyst performance the MgO samples must be freshly calcined before use, or kept in a sealed environment, away from atmospheric H<sub>2</sub>O and CO<sub>2</sub> [3]. This is in agreement with our observation that MgCO<sub>3</sub> must be completely removed by calcination in order to achieve the best catalyst performance.

Finally, the reusability of the MgO-CBC was investigated by recovering the catalyst after the reaction of benzaldehyde with



**Fig. 12.** The TGA (i) and DTG (ii) curves of MgO cooled under different conditions: (a) fresh MgO cooled down to 280 °C in furnace; (b) sample a cooled to room temperature in static air; (c) sample a cooled to room temperature in CO<sub>2</sub> and H<sub>2</sub>O vapour; (d) sample a cooled to room temperature in N<sub>2</sub> and H<sub>2</sub>O vapour.

2-butanol. The recovered catalyst was washed with acetone ( $3 \times 10$  ml), refluxed in water (10 ml) for 3 h, dried at  $110^\circ\text{C}$  (24 h) and finally calcined at  $450^\circ\text{C}$  for 2 h. The surface area of the material ( $287 \text{ m}^2 \text{ g}^{-1}$ ) was found to be the same after the reactivation procedure as it was before the initial run (Table 1). When the reactivated MgO was used as a catalyst for the same reaction, the performance (conversion: 88.0%; selectivity: 98.7%) was the same as that seen for the first reaction (Table 3, entry 1).

#### 4. Conclusions

A simple synthetic procedure was shown to produce high surface area MgO catalysts that have a very high activity and selectivity for the MPV reaction compared to previous studies. Although high surface area MgO has been synthesized previously using relatively complex techniques (e.g. CVD, sol-gel procedures and aerogel synthesis) [34–40], and very good multi-component base catalysts have been identified [12–27], the simplicity of the methodology presented here offers several advantages. We have demonstrated that using this approach, high surface area MgO can be prepared from a wide range of starting materials, without the need for expensive equipment or reagents. We have also shown that the catalysts can be reused after a simple reactivation procedure.

While there is a need to develop advanced materials for use as base catalysts in specialist applications, for many important synthesis reactions, such as aldolisation, alkylation, Meerwein–Ponndorf–Verley reduction, Wadsworth–Emmons addition, Knoevenagel and Michael condensations, the methodology described here can be used to prepare simple, high surface area MgO catalysts that can be used as an alternative to environmentally unfriendly aqueous base. This can help to reduce the amount of toxic aqueous waste produced that is expensive to clean up. The simplicity of the synthesis procedure gives these materials the potential for widespread use in a variety of applications.

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